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LASER MIXING OF TITANIUM ON SILICON CARBIDE

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ABSTRACT

We have used excimer laser surface processing to melt and mix single Ti layers into the surface of polycrystalline SiC substrates. The mixing of Ti into the surface is very rapid and efficient. Examination of Rutherford backscattering (RBS) data for different mixing conditions shows the formation of a preferred composition at the Ti-substrate interface which propagates from the interface with further mixing. Reconstruction of the RBS spectrum indicates that the composition of the layer is $Ti_{45}C_{37}Si_{18}$. X-ray diffraction demonstrates the formation of Ti silicides and carbides in the surface region. Profiling of C in both mixed and uncoated samples by 5 MeV He^+ scattering demonstrates that laser processing of the SiC does not cause major changes in the stoichiometry of the substrate material.

INTRODUCTION

The use of structural ceramics in high temperature engineering applications is limited by the tendency of these materials to fracture in tension without significant plastic deformation . Cracks, originating in surface flaws, propagate rapidly into the material, causing brittle failure in the bulk. Attempts to reduce this effect using ion implantation have concentrated on creating a compressive zone through radiation damage and alloying effects in the near surface region[1]. Excimer laser radiation has been used to alloy Ni into SiC and Si_3N_4 ceramic materials with an increase in strength found[2,3]. In all these experiments, the surface layers produced have been partially amorphous or at least highly disordered. We have chosen to use a more reactive metal, Ti, in laser mixing experiments on SiC. The strong affinity of Ti for both Si and C in the substrate is expected to lead to the formation of chemically stable species despite the very high rates of solidification experienced in excimer laser processing.

EXPERIMENT

A single layer of Ti was evaporated onto polished polycrystalline SiC substrates using an e-beam evaporation system with a base pressure of the order of 10^{-8} torr. Although the samples were kept in a desiccator, no extraordinary measures were taken to protect them from oxygen exposure. The samples were processed within one day of evaporation using an excimer laser operating at 248 nm (KrF). Because the output of the laser is spatially nonuniform, a multi-element refractive beam homogenizer was used to create uniform illumination on the workpiece. The sample was translated at a uniform speed in front of the beam so that at a repetition rate of 5.0 Hz, there was an 80% overlap. Thus each position on the sample received 5 pulses of laser radiation. In order to explore the effect of the number of pulses on mixing, some samples were treated with a second pass to provide 10 pulses/position. The beam energy was controlled using a feedback system so that pulse to pulse variation was less than 10%. A fluence of 1.2 J-cm^{-2} was used in all the experiments.

Rutherford Backscattering Spectrometry (RBS) was used to determine the mixing of the surface. RBS spectra were obtained at the Los Alamos Ion Beam Materials Laboratory using 2.0 MeV He^+ ions. Figure 1 shows the spectra for the as deposited Ti layer and for the same sample after processing with 5 and 10 pulses of laser radiation. After processing, Si has diffused to the surface and Ti into the substrate. There is little (<20%) loss of Ti as determined by integration of the Ti peak. It is apparent that most of the reaction has taken place after 5 pulses,

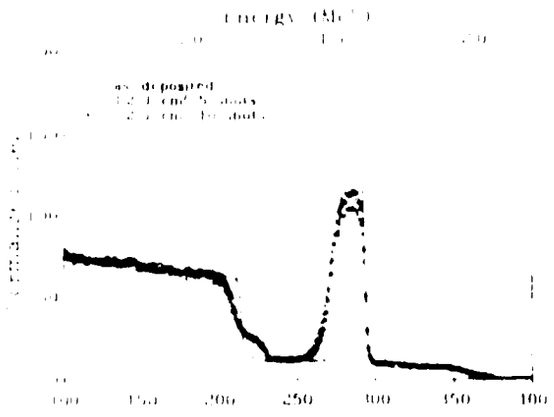

Figure 1. RBS spectrum of as deposited and laser mixed Ti on SiC. Markers are for position of surface peak of Ti, Si, and W. Mixing is evident from the diffusion of Si to the surface and the diffusion of Ti into the substrate.

although some further mixing occurs after the additional 5 pulses. Further evidence of this can be seen in figure 2, which shows the 5.0 MeV backscattering spectrum. It shows that the C concentration in the surface region is relatively constant for the two cases, the primary difference being the thickness of the reacted layer. A fit to the RBS data using RUMP gives a composition of $Ti_{45}C_{37}Si_{18}$ in a uniform layer of thickness 200 nm. Because there have been reports of C evaporation under excimer laser radiation[ ] and we have seen evidence of C loss in laser treated steels[ ], 5.0 MeV backscattering measurements were also made on polished SiC treated at various fluences. There was no evidence of decomposition until the fluence was raised to 3.0 $J\text{-}cm^{-2}$, well higher than the fluences used in the mixing experiments.

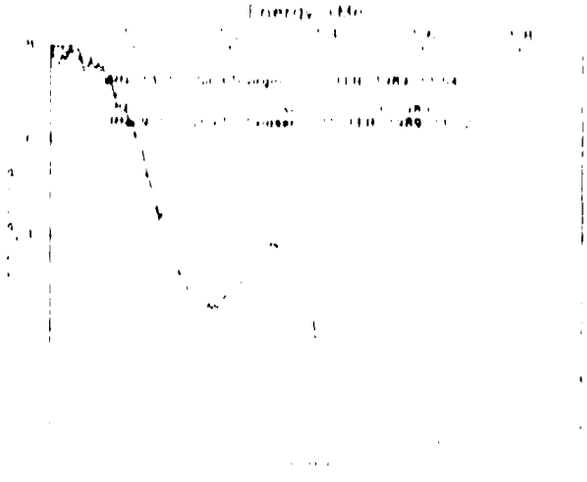

Figure 2. 5.0 MeV He^+ backscattering data for as deposited and laser mixed Ti on SiC. Marker shows position of C surface peak. Surface C contamination is evident and is formation of alloy with constant C concentration in the mixed zone.

X-ray diffraction data were taken at grazing incidence (3°) using monochromatized Cu Kα radiation at 1.5406 Å and a position sensitive detector set to acquire 2θ over 120°. The sample was held stationary. A polished, unprocessed SiC sample showed diffraction lines at expected intensities for SiC as well as WC (the W is a binder in the SiC). Table I shows the most significant observed diffraction lines and assignments made. There were no significant differences between the data taken from samples processed with 5 and 10 pulses. In addition to the SiC and WC lines seen in the untreated samples, a number of new diffraction lines were found. Analysis of this pattern, allowing for overlap with the previously observed lines, indicates the formation of $TiSi_2$ and TiC. The strength of the line at d = 0.911 Å was anomalous given these assignments, but no pattern could be found which supported another assignment. A number of other lines were also observed, but no evidence was found for the existence of any Ti oxide phase.

d Spacing	Intensity	$TiSi_2$	TiC	SiC	WC
2.635	20			2	
2.851	5				3
2.518	100		2	1	1
2.358	24	1			
2.183	8	4	1	5	
2.156	3	2			
1.888	11	3			2
1.545	26		3	3	
1.443	3	5			
1.326	10		4		
1.291	27			4	
1.239	5				4
0.989	3		5		
0.911	15		6		

Table 1. Observed X-ray diffraction lines and intensities. Numerical assignments refer to the relative strengths of the lines for the individual compounds.

DISCUSSION

The RBS and high energy backscattering data demonstrate that mixing has occurred and that the amount of mixing is relatively insensitive to the number of pulses. In fact, other experiments demonstrate that mixing is quite complete even after two pulses of laser radiation. While there is a strong driving force for mixing, there is an equally strong inhibition of mixing beyond a certain point in this system. Similar experiments on AISI 304 stainless steel demonstrate that diffusion of substrate material to the surface continues to occur with larger numbers of pulses[4]. In figure 3, we show a simplified version of the ternary phase diagram for this system[5] with the composition of the mixed layer indicated by the shaded dot. From this diagram, one would expect that the mixed layer would consist of SiC, TiC, and $TiSi_2$. In fact, TiC and $TiSi_2$ appear in the diffraction pattern along with SiC which would be expected in any case from substrate reflections. Apparently, further outdiffusion of Si from the substrate material is inhibited by the formation of the the surface layer. This could be either

because the strength of the covalent Si-C bond in the substrate maintains the integrity of the material unless the temperature is quite high or because the stoichiometric silicide and carbides stabilize the layer against further Si diffusion. The phase diagram indicates that further Si from the substrate could easily be accommodated at equilibrium. However, the existing composition is determined in part by the kinetics of rapid solidification experienced by the surface layer. A simple one-dimensional heat flow calculation has shown that the cooling rate in SiC is of the order of 10^{10} K-sec^{-1}[6], high enough to produce metastable or amorphous phases. We do not know the relative phase composition of the surface layer and it is possible that although the phases present are consistent with the equilibrium diagram, their relative composition is not.

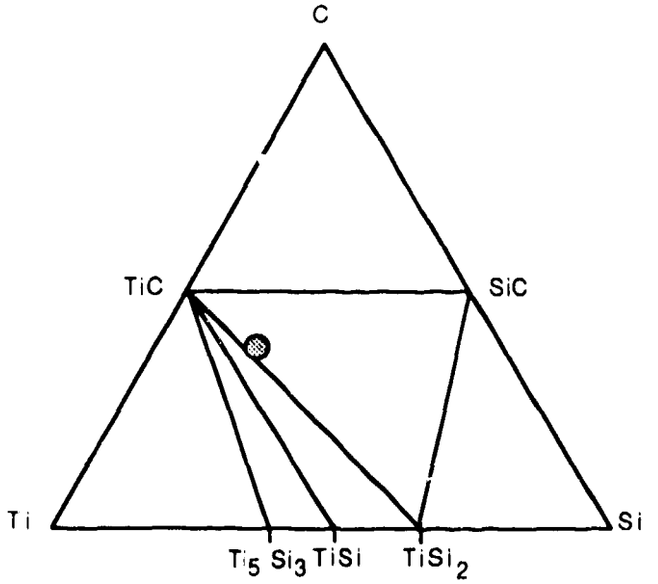

Figure 3. Ternary Phase Diagram of the Ti- Si-C system. The composition of the laser mixed layer is given by the shaded area.

CONCLUSIONS

We have found that excimer laser mixing of Ti on SiC substrates proceeds rapidly with the formation of an apparently preferred composition of SiC, TiC, and $TiSi_2$. The effects are due entirely to the mixing phenomena and not to decomposition of the substrate material. The mechanical properties of these layers is under study.

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